

THE ADSORPTION OF CERTAIN VA-
PORS BY CHARCOAL AT VARIOUS
TEMPERATURES UP TO AND
ABOVE THEIR CRITICAL
TEMPERATURES

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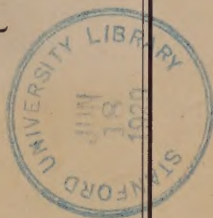
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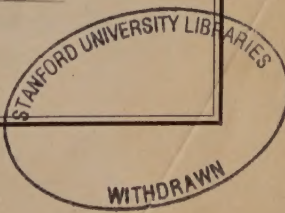
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THE ADSORPTION OF CERTAIN VAPORS BY CHARCOAL AT VARIOUS TEMPERATURES UP TO AND ABOVE THEIR CRITICAL TEMPERATURES

It is perhaps safe to state that no one property of a solid substance has been more persistently studied through so long a period as has been the property of solid porous bodies to adsorb gases and vapors. The phenomenon of the adsorption of gases and vapors by charcoal was originally discovered independently by Scheele¹ and by Fontana¹ in 1777. In the century following much was contributed which deals with the general qualitative side of adsorption. It was not until the beginning of the present century and more particularly with the advent of poison gas warfare and the consequent demand for gas mask adsorbents that an intensive study of charcoal and its properties was undertaken. Since then many investigations have been made and a number of theories have been put forth in the attempt to explain the mechanism of adsorption and to deduce laws governing it.

Although a vast amount of data has been collected, dealing with the adsorption of many substances by charcoal, the results are not satisfactorily comparable for many reasons. In the first place, the many adsorption experiments have been performed on charcoals obtained from various sources and of varied past history, as regards the temperature of formation, mode of activation, the temperature and thoroughness of evacuation, and the nature and effect of the vapors previously adsorbed. The materials from which the charcoal is produced contain mineral matter which on charring is chiefly transformed to metallic oxides. These oxides also possess their own specific adsorption powers. The magnitude of the adsorption of a vapor by ordinary charcoal will, therefore, be affected by, and vary with, the nature of the mineral matter. It will also vary with the porosity of the charcoal.

The object of the present investigation is to make a systematic study of the adsorption of a large number of vapors by a uniform sample of steam-activated, "acid washed, acid free" coconut charcoal. The charcoal was kindly prepared for us by the Carbide and

¹ Ostwald, *Lehrb. d. allgemein. Chemie*, I. Auf., 1, 778 (1884).

Carbon Chemicals Corporation. In this work we intend (1) to determine the adsorption isotherms for each vapor over the widest possible range of temperature, including temperatures higher than the critical temperature, when possible; (2) to determine the relation between the magnitude of adsorption and the corresponding temperatures of the liquids; (3) to determine the influence of certain physical properties,—molecular volume, surface tension, viscosity, compressibility, etc., upon the amount of adsorption. (4) By employing vapors belonging to definite homologous series, it may be possible to arrive at some fundamental generalizations involving the influence of the nature of the molecule — its volume, configuration and mass, as well as the electrical nature of the substituents in the molecule, upon the ease with which the vapor is adsorbed.

The present paper is limited to the study of the adsorption of the vapors of water, methyl and ethyl alcohol, ammonia and methyl amine. Since the work is of a preliminary nature anticipating some now in progress, we shall only attempt to present the principle results and leave much of the theoretical discussion to later papers.

MATERIALS AND APPARATUS

A high-grade sample of absolute, acetone-free methyl alcohol was first refluxed for several hours over metallic calcium and then distilled through a tall fractionating column. It was next refluxed over pure anhydrous silver nitrate to remove aldehydes and again distilled. This distillate was subjected to a final distillation from metallic calcium. In each distillation only the constant boiling middle portion was retained. The ethyl alcohol was first allowed to stand over fresh quick lime for several weeks; it was then decanted and distilled, the subsequent purification was made in the same manner as with methyl alcohol. The water used was regular conductivity water, distilled from an alkaline permanganate solution, and collected hot to avoid the presence of dissolved gases. The ammonia was taken directly from a tank of anhydrous ammonia and passed over solid KOH to remove any traces of moisture. The purity of the ammonia gas was further tested by allowing a slow stream of the gas to bubble into a gas burette filled with dilute H_2SO_4 . Although the flow was allowed to continue for a considerable time, no measureable volume of an insoluble gas was detectable. A quantity of Eastman's 33 percent aqueous methyl amine was placed in a large separatory funnel closed tightly with a rubber stopper carrying a tube with a stop-

cock. The stopper was sealed with DeKhotinsky cement, the space above the liquid was opened to the vacuum pump for a few minutes and the stopcock was then closed to prevent access of air. The free amine gas was obtained by allowing the solution to fall drop by drop on a large quantity of solid NaOH which took up the water. The amine was further dried by passing through a length of several feet of closely packed pieces of solid KOH. The entire system, in which the amine was generated, was first evacuated, repeatedly filled with the amine and evacuated, before any of the gas actually used in the experiments was collected. The ash content of the charcoal amounted to 0.28 per cent of the total weight; the size of the particles used ranged from 12 to 20 mesh.

The loss in weight in outgassing the charcoal was determined by evacuating a weighed sample of charcoal under the same conditions as those employed in a regular experiment. When the pressure had remained constant at about 0.001 mm., or less, for several hours the tube was sealed off and weighed. The mean of three such independent determinations corresponded to a loss of 2.50 per cent; this value was used in correcting the weight of all samples of charcoal to obtain the actual weight of carbon used. The density of the charcoal was determined by evacuating a weighed sample at 500° until the pressure remained constant at 0.001 mm., or less, for several hours. The tube was then sealed, cooled and weighed again. The capillary was broken under hot, recently boiled distilled water, allowing the water to fill the pores of the charcoal. After permitting the temperature to become constant by immersing in a thermostat at 25°, the level of the water was adjusted to a given mark and the bulk weighed. The charcoal was then removed, the tube was filled to the mark with water at 25° and again weighed. The mean of four such determinations gave a value of 1.80 for the density of the charcoal used. This value was considered sufficiently accurate for calculating the "dead space."

APPARATUS

The apparatus used was a slightly modified form of that used by Patrick and McGavick² in their study of the adsorption of SO₂ by silica gel. The apparatus was entirely of glass and all stopcocks were of the mercury seal type. The whole apparatus was set up in a large double-walled wooden air bath, fitted with two glass doors to permit readings without disturbing the temperature within. Four sets of lamp banks were placed between the walls to

² Patrick and McGavick, J. Amer. Chem. Soc., 42, 946 (1920).

furnish heat, and two Mazda lamps were placed at convenient points within the bath to provide illumination. A high-speed fan at the top circulated air over the lamps and drew the heated air up through holes bored in the false bottom. The temperature was electrically controlled at the desired temperature to $\pm 0.05^\circ$ by means of a mercury thermoregulator whose length was almost as great as the inside height of the bath. Still more accurate control was obtained when desired by hand regulation for a few minutes just before taking a reading.

The bulb for measuring the volume of the vapor admitted was calibrated with mercury for every 10° between 20° and 80° , and

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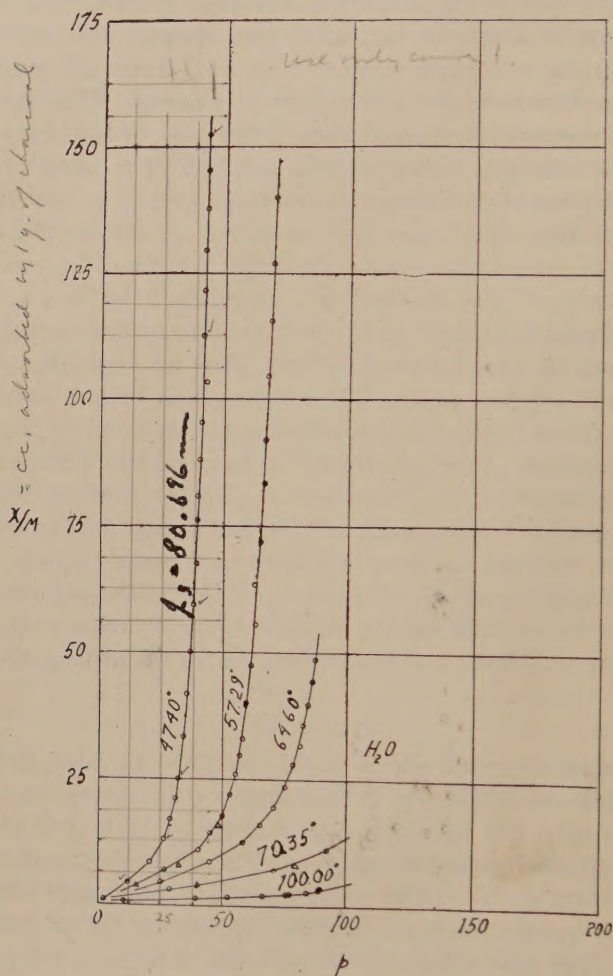


Fig. 1

for lower values ⁶ of relative humidity
 ϕ/p_s

a curve was plotted from which the volume could be read at any desired temperature between these limits. The charcoal bulb and all connecting tubing were accurately calibrated by means of mercury. During the evacuation the charcoal was heated by means of a small resistance furnace at a temperature of $500^{\circ} \pm 10^{\circ}$. The temperature of the charcoal during an adsorption measurement was maintained constant by immersion in the vapor of a boiling liquid. The boiling flask was fitted with a return condenser and a ground glass stopper through which were sealed four tubes. The large central tube was filled with mercury in which was immersed the adsorption bulb, thus insuring uniform temperature through-

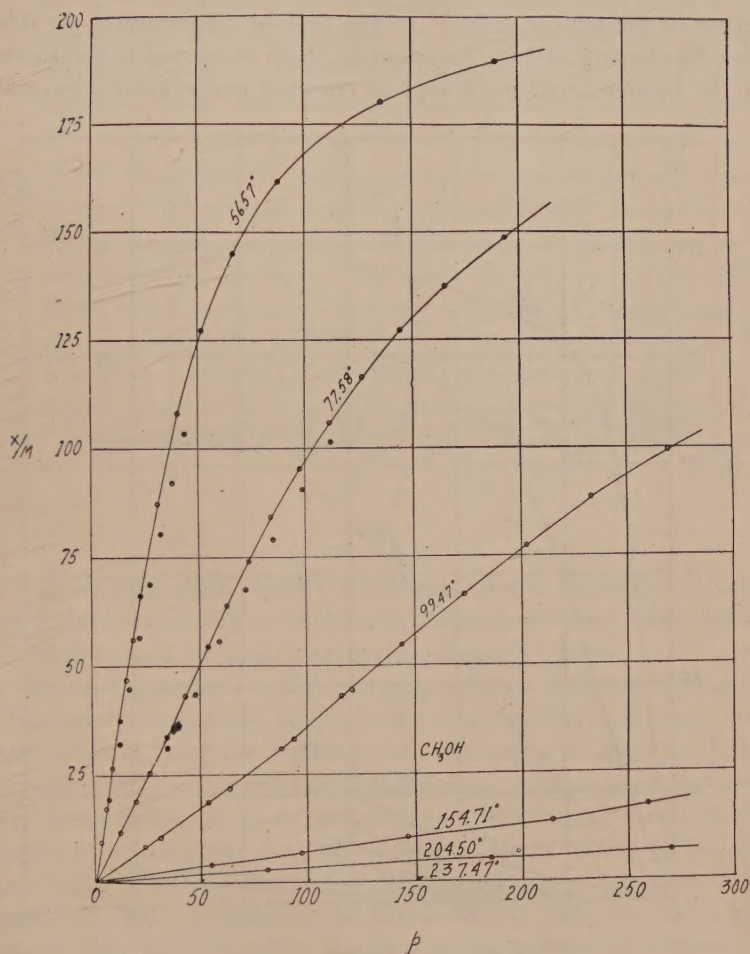


Fig. 2

out the bulb and a part of the stem. Another tube containing a few drops of mercury for thermal contact held the thermometer by which the temperature of the charcoal was read. The two remaining tubes were used as leads for the current employed to heat the coil of nichrome wire immersed in the boiling liquid. The heating current was regulated by means of a small resistance in series with the coil. In this way the temperature of the charcoal bulb could be maintained constant for indefinite periods, subject only to barometric fluctuations. When these fluctuations became considerable the vapor pressure of the boiling liquid was hand-controlled by a pressure device attached to the top of the condenser. By means of this it was possible to control the temperature of the bulb to $\pm 0.02^\circ$ at any desired temperature. In this way the charcoal and the thermometer, both immersed in the vapor of the boiling liquid were kept at constant temperature. Several

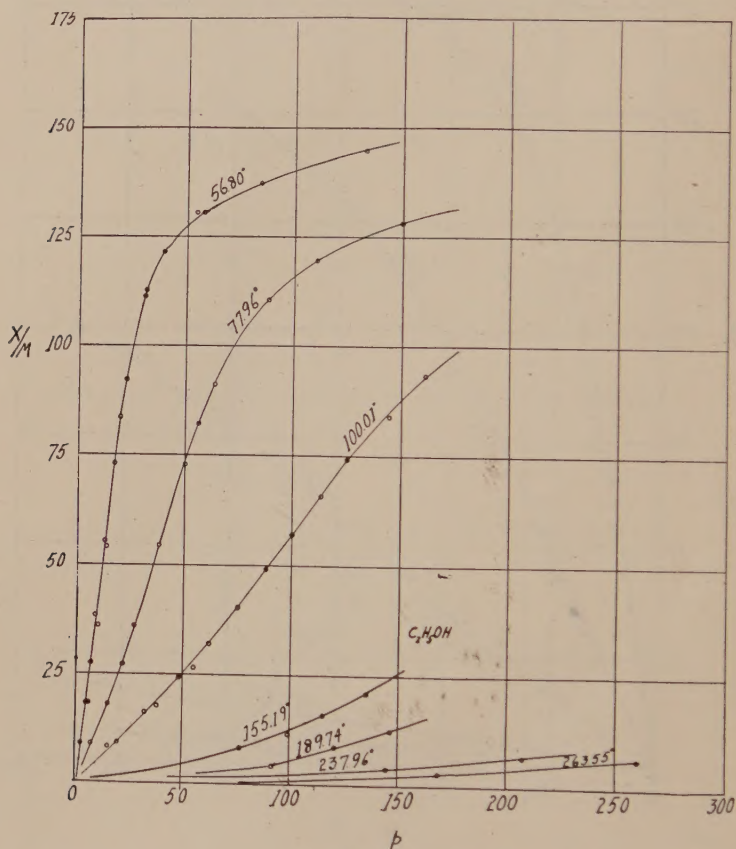


Fig. 3

short-range thermometers, reading directly to 0.1° and estimable to 0.02° , were calibrated against Bureau of Standards thermometers and used in the boiling flask.

The mercury wells which controlled the levels of the mercury in the manometers were suspended from pulleys by flexible wires. These wires were attached in turn to sensitive ratchets which made possible a close adjustment of the mercury levels. All pressure readings were made with the aid of a precision cathetometer, readable by means of a vernier to 0.05 mm.

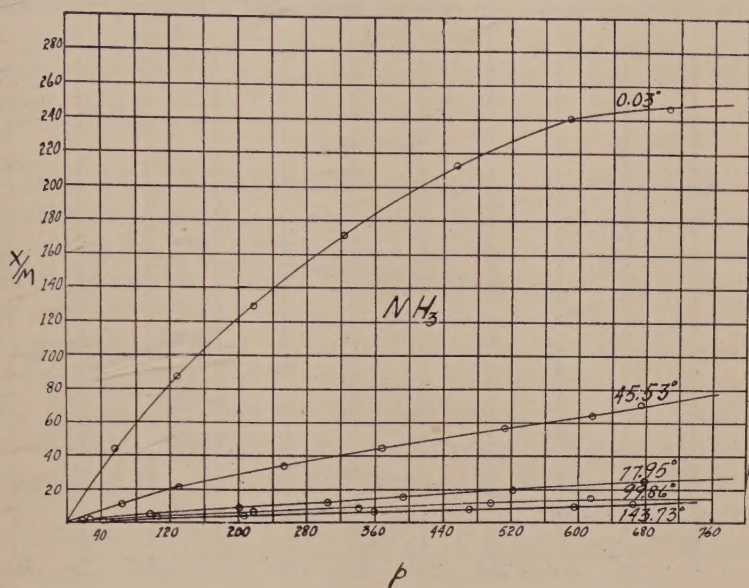


Fig. 4

The pumps used for the evacuation of the charcoal consisted of a Cenco oil-pump in series with a Kraus mercury pump and a Langmuir high vacuum mercury condensation pump.

Before beginning a series of determinations a known weight of charcoal was placed in the bulb, the small resistance furnace was put in place, and the charcoal was evacuated at 500° until the pressure had become less than 0.00005 mm. The charcoal was then permitted to cool to room temperature and a large volume of the vapor to be used was admitted. After the vapor had stood in contact with the charcoal for a few hours, the evacuation was repeated. This procedure was deemed wise, since Harned³ has shown that reproducibility is not obtained unless the charcoal is

³ Harned, J. Am. Chem. Soc., 42, 372 (1920).

flushed out with the vapor which is to be investigated. When the pressure at 500° has again been reduced to less than 0.00005 mm. the charcoal bulb is shut off. If after standing for several hours, or, as it usually happened, over night, the pressure was still less than 0.00005 mm., the boiling flask was then put in place, the charcoal was heated to the desired temperature, and a known, accurately measured volume of the vapor was admitted.

The time required after the admission of the vapor to establish adsorption equilibrium varied with the different vapors and also with the temperature. In general, it required a longer time at the

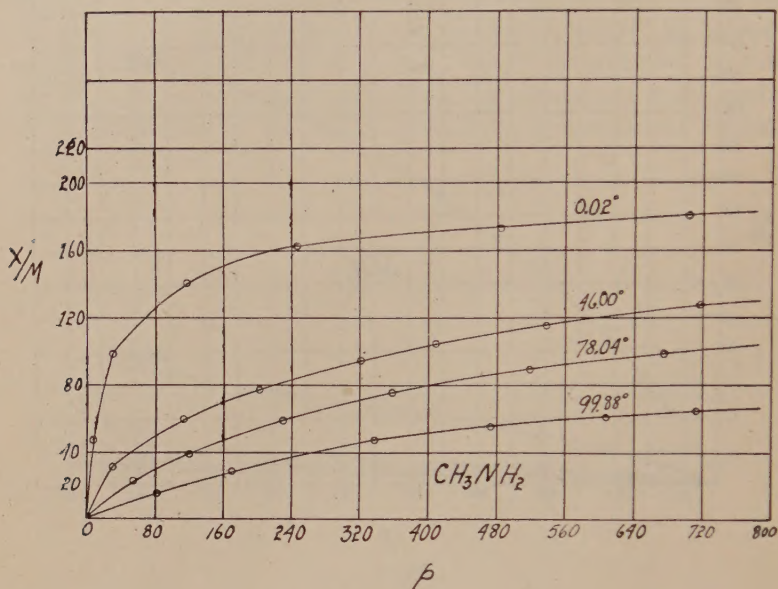


Fig. 5

higher than at the lower temperatures. Equilibrium was assumed to exist when consecutive readings taken at half-hour intervals did not vary by more than 0.05 mm. When this constant pressure had been obtained another sample of the vapor was admitted. This procedure was repeated until the equilibrium pressure became equal to the saturation pressure.

All pressure readings were reduced to 0° , 45° latitude and sea level. All volumes were reduced to normal conditions. The volume of the vapor adsorbed was calculated by subtracting the volume of the vapor in the "dead space," i.e., the volume of the unadsorbed vapor above the charcoal and in the connecting tubes, from the total corrected volume transferred from the measuring

bulb. The volume of the dead space was obtained by subtracting the actual volume of the charcoal from the volume of the bulb and the connecting tube.

A complete set of adsorption data has been obtained for each vapor within the pressure and temperature limits measurable. We have tabulated for each temperature studied the volume of vapor (N.T.P.) in c.c. adsorbed by 1 g. of charcoal, x/m , and the corresponding equilibrium pressures, p . Owing to the bulkiness of the data these tables will be omitted in this paper. The results obtained are best shown graphically in the plots of the natural isotherms, Figs. I to V. A large scale plot was also made and the data necessary for the subsequent calculations were read from these curves.

DISCUSSION

In general, the isotherms are typical of those obtained in all ordinary adsorption processes. They show that at the lower temperatures the adsorption capacity is quite large, and very considerable amounts of vapor are adsorbed with only a small increase in pressure. With increasing amounts of vapor added the pressure changes become more marked, the curves bending sharply toward the pressure axis, and in some cases running almost parallel with it. As the temperature is increased the isotherms become less curved, and at still higher temperatures they become straight lines throughout the whole pressure range. The decrease in adsorption with rise in temperature is so rapid that by the time the critical temperature is reached the quantity of vapor adsorbed becomes exceedingly small. Methyl alcohol is practically unadsorbed at its critical temperature, but ethyl alcohol and ammonia vapors show a small but definite adsorption at temperatures even above their critical temperatures. The adsorption of water vapor at 100° was so slight that it was not considered worth while to continue the study at higher temperatures. It was found to be impossible to study the adsorption of methyl amine at temperatures above 100° . At this temperature the amine is apparently stable, but at higher temperatures it is catalytically decomposed by the charcoal. This was evidenced by the fact that when a sample of the amine was admitted to the charcoal at 143° , the pressure at first naturally decreased for a short time, and then began to increase and continued to do so during the next 24 hours without showing any tendency to reach an equilibrium value. Thinking that perhaps a leak had developed in the apparatus, the charcoal was again evacuated and allowed to stand for several hours. No appreciable

increase in pressure was observed. When a second sample was admitted the former behavior was repeated. The temperature of the charcoal was then raised to 182° , and at this temperature the rate of decomposition, as indicated by the rise in pressure, was found to have increased almost 10-fold.

As with many other properties, the adsorption of water vapor shows striking anomalous characteristics, Fig. I. The isotherms for water are concave toward the concentration axis, instead of toward the pressure axis. Even at the lowest temperature studied the equilibrium pressure increases rapidly at first, but as more vapor is added the rate of increase diminishes, until finally, the addition of more than 15 cc. (N.T.P.) of vapor produces only a few 0.1 mm. rise in pressure. This anomalous behavior of water vapor has been observed by Hulett and Lowry.⁴ They seek to explain it on the assumption that water vapor is not adsorbed, but is absorbed by the charcoal. That is, because of its high surface tension, the tendency is for the vapor to be condensed in the capillaries rather than to be held by the surface attraction of adsorption. The concavity of the isotherm to the concentration axis is explained as being due to the fact that the smaller capillaries, which give the lower vapor pressures, are filled first and more rapidly so than are the larger ones. Consequently, the pressure increases more rapidly at first as vapor is added than it does when the larger capillaries are being filled.

Lowry and Hulett⁴ have reported a sharp break in the isotherms for water. In our first experiment at 57.25° we actually did observe such a discontinuity, but all attempts to duplicate the observation, either at the same, or at higher or lower temperatures, resulted in smooth, continuous, normal curves. We concluded, therefore, that our first observation was in error, probably due to the entrance of a small amount of air through a stop-cock into the adsorption bulb. This would readily account for the peculiar shape of the curve, since a small amount of an only slightly adsorbed gas, like air, would produce a considerably greater increase in pressure than would an equal volume of water vapor: Upon further additions of water vapor the curve should follow a course approximately parallel to its normal course, but it should be shifted along the pressure axis to regions of higher pressure.

The relation which has been used most frequently to express the relation between the magnitude of adsorption and the equilibrium pressure is the empirical equation proposed by Freundlich:⁵

⁴ Lowry and Hulett, *J. Am. Chem. Soc.*, 42, 1393, 1408 (1920).

⁵ Freundlich, *J. Chem. Ind. Kolloide*, 3, 212 (1909).

$$x/m = a'p^{1/n}, \quad (1)$$

Here x/m and p have their usual significance, and a and n are constants which depend on the nature of the adsorbent, on the nature of the adsorbed substance, and on the temperature. It is evident that a represents the volume of gas or vapor adsorbed at unit pressure. The logarithmic form of (1), viz.,

$$\log x/m = \log a + 1/n \log p, \quad (2)$$

is linear with respect to $\log x/m$ and $\log p$, and $1/n$ is the slope of the curve.

If the Freundlich equation (1) is applicable to the vapors studied, we should obtain for each vapor studied a system of straight lines when the values of $\log x/m$ are plotted against the logs of the corresponding equilibrium pressures, p . We have plotted these double-log isotherms and have found that the Freundlich equation is applicable to methyl alcohol and to ammonia, except in regions of high pressure and high concentration, that is, near saturation. While these double-log isotherms for ethyl alcohol are fairly straight, they deviate markedly for water vapor and for methyl amine. This might be expected for water, because of the shape of its natural isotherms. Perhaps the most significant thing to be observed in the double-log isotherms is the fact that the different isotherms parallel each other over those pressure ranges for which equation (2) is valid. This is especially true for methyl alcohol. In other words, the slope, $1/n$, changes but little with the temperature over this range of almost 150° .

Miss Homfray⁶ has found that the Freundlich equation expresses well the results of her observations on the adsorption of A, N₂, CO, CH₄, C₂H₄ and CO₂ by charcoal at pressures up to one atmosphere. She has found also that the value of $1/n$ increases from about 0.2 at low temperatures and approaches unity as the temperature is increased. Richardson⁷ has studied the adsorption of CO₂ and NH₃ by charcoal to pressures as high as 300 mm. He finds that equation (2) gave fair agreement over a limited pressure range, but not throughout the entire range studied. Schmidt and Hinteler⁸ deduced an equation for the isotherm which may be put in the following form: $\log p - \log x/m - B \cdot x/m = K$. If this expression is applicable, the plot of $\log p - \log x/m$ against x/m should give a straight line. While such a

⁶ Miss Homfray, *Z. physik. Chem.*, **74**, 129 (1910); *Proc. Roy. Soc., London*, **84**, 99 (1910).

⁷ Richardson, *J. Am. Chem. Soc.*, **39**, 1828 (1917).

⁸ Schmidt and Hinteler, *Z. physik. Chem.*, **91**, 103 (1916).

curve was actually obtained for benzene, the curve obtained for CS_2 deviated somewhat from a straight line. They found that the equation did not apply for vapors of hexane, acetone, methyl and ethyl alcohols and water. We also have tested the same equation with our vapors and the curves obtained were so far from linear that it is apparent that the equation is not applicable to the adsorption of the vapors which we have studied. Schmidt and Hinteler also deduced a second equation, but this and the one so successfully used by Patrick and his students⁹ are modifications of the Freundlich equation and they should apply to all vapors for which the latter equation (1) is valid. Geddes¹⁰ has used an empirical semi-log equation: $x/m = a \pm b \log p$. Except at low pressures, he found this to hold well for the adsorption of CO_2 by charcoal. We have tested this equation by plotting the values of x/m against the corresponding values of $\log p$. It was apparent from the curves obtained that this semi-log equation is only satisfied in the middle portions of some of the curves. Even with these there is a very marked curvature at the beginning of most of the curves, and those at the lower temperatures show some curvature in the upper portions also. In those regions of concentration and pressure where the curves do approximate straight lines the curves are parallel.

Among the equations which have been used to express the relation between the temperature and the amount of gas adsorbed at constant pressure is that given by Miss Homfray:⁶

$$-\frac{dT}{d \log C} = K. \quad (3)$$

Here C is expressed in percent by weight of adsorbed substance calculated on the total weight of the adsorbent plus adsorbed substance. Miss Homfray found for all gases which she studied that at low pressures, and for A and N_2 at all pressures, the straight lines obtained on plotting T against $\log C$, when extrapolated to $\log C = 2.0$, or 100 percent concentration of gas, gave the boiling point of the liquefied gas at that pressure. She further states that, for the different gases studied, the values of K for the same pressure increase uniformly with increasing complexity of molecular structure. Moreover, the order is the same as that of the molecular refractions and molecular volumes of the respec-

⁹ McGavack and Patrick, *J. Am. Chem. Soc.*, 42, 946 (1920); Patrick and Davidheiser, *ibid.*, 44, 1 (1922).

¹⁰ Geddes, *Ann. Physik*, 29, 797 (1909).

tive gases. Another equation representing isobaric relations is that of Freundlich;⁵ this has the form,

$$\log (x/m)_t = \log (x/m)_o - (\zeta - \xi \log p)t. \quad (4)$$

Here, $(x/m)_t$ and $(x/m)_o$ are the masses adsorbed per gram of charcoal at the temperatures t° and 0°C , respectively, p is the pressure, and ζ and ξ are constants which are related to the $1/n$ and x/m of equation (1), thus

$$\zeta = - \frac{d \log x/m}{dt}, \text{ and } \xi = \frac{d (1/n)}{dt}. \quad (5)$$

According to Miss Homfray's equation (3) straight lines should be obtained when the values of $\log C$ are plotted against T . Likewise, we should obtain similar linear curves when, as from (4), the values of $\log x/m$ are plotted against t° . Both methods of plotting were tried, but in neither case did we find the equations valid for the vapors which we used. Methyl amine, ammonia and ethyl alcohol gave fairly straight portions at the lower, but deviated markedly at the higher temperatures. Exactly the reverse was true for the isobars for water vapor, while those for methyl alcohol only approached the linear property in the middle of the plot. We have also plotted the $\log x/m$ values against the reciprocals of the corresponding absolute temperatures. These plots give fairly straight lines for water vapor and the two alcohols, but not for ammonia and methyl amine.

The plots of the isosteres were obtained from the large plots of the isotherms by reading off the pressures corresponding to certain definite values of x/m from each isotherm. These were plotted in different ways. When the pressure is plotted against the temperature the vapors give a series of semi-fan-shaped curves, the one exception being water vapor. The isosteres for water approximate straight lines, showing that the pressure varies almost directly as the temperature when the quantity adsorbed is constant. All of the other curves show a less rapid increase in pressure at the lower than at the higher temperatures for equal increments of temperature.

Freundlich's equation for the isostere is written,

$$\frac{dT}{d \log p} = n (\zeta - \xi \log p). \quad (6)$$

In this n is the constant of equation (1), and ζ and ξ have the same significance as in (5). At higher temperatures, when $1/n$

becomes unity, ξ becomes zero and the above equation by integration becomes,

$$\log P_t = \log p_o - \xi't. \quad (7)$$

According to (6) the ratio $d \log p/dT$ should not be constant, but should increase as the temperature falls. We have accordingly plotted the values of $\log p$ against the temperature. With the possible exception of the isosteres of CH_3NH_2 , all of the curves were quite straight and parallel at the lower temperatures, but some of them show deviations at higher temperatures. This is in harmony with the principle of the Freundlich equation (6) in which $\xi = d(1/n)/dT = 0$, and therefore, with the condition that $1/n$ be practically independent of the temperature.

When the quantity of the adsorbed vapor, a , is maintained constant, the Williams¹¹ equation for the isostere,

$$\log \frac{a}{C} = B - \frac{A}{T}, \quad (8)$$

indicates that the plotting of $\log C$, or the proportional $\log p$, against the reciprocal of the absolute temperature should give a straight line. Coolidge¹² found this to be true for a number of substances, including CH_3OH and H_2O . This test was applied to our data, but the approximation to a linear relation was no closer than that obtained when the temperature, rather than its reciprocal, is used as one of the variables.

Ramsay and Young have found that the boiling points of two liquids are related by the expression,

$$\frac{T_o}{T} = \frac{T'_o}{T'} = R (T_o - T'_o). \quad (9)$$

In this T and T' are two absolute temperatures read from any one isostere at any two pressures, T_o and T'_o are the absolute temperatures at which any saturated vapor, taken as a standard, has the same pressures, and R is a constant. The reference vapor chosen was that of ethyl alcohol. Values of T_o/T for various pressures along a given isostere were calculated and plotted against T_o . Straight lines should be obtained, if the law applies. The law does not appear to apply as to the vapors of ammonia and methyl amine. The curves for methyl and ethyl alcohol for limited ranges indicate an approximation to the law. The curves for water vapor are quite straight, but the range of T_o values for

¹¹ Williams, Trans. Faraday Soc., 10, 167 (1914); Proc. Roy. Soc., London, 96A, 287 (1919).

¹² Coolidge, J. Am. Chem. Soc., 46, 596 (1923).

each curve is small, due to the low vapor pressure of the water at the temperature at which the air-bath was maintained. One interesting fact was observed in making these calculations, namely, at the higher concentrations, (say $x/m = 50$ cc.), the ratio of T_0/T is practically constant along a given isostere. This was particularly true for the two alcohols and water.

It was thought that the law of corresponding states might be found to apply to the adsorption of vapors. That is, under the same pressure equal amounts of different vapors will be adsorbed at temperatures which are equal fractions of the critical temperatures of the vapors. To test this relation the fractions of the critical temperature T/T_c corresponding to certain values of p and x/m were calculated for the five vapors studied. The results are indicated in the following Table.

RELATION BETWEEN ABSORPTION MAGNITUDES AND THE CORRESPONDING TEMPERATURES

$\frac{x}{M}$	p	$\frac{T}{T_c}$				
c. c.	mm.	H ₂ O	CH ₃ OH	C ₂ H ₅ OH	NH ₃	CH ₃ NH ₂
5	20	0.511	0.746	0.760	0.765	0.854
5	30	0.524	0.772	0.786		
5	40	0.533	0.793	0.809	0.815	
5	50	0.542	0.811	0.826	0.830	
10	20		0.708	0.719	0.723	0.812
10	30	0.502	0.728	0.740		0.841
10	40	0.512	0.743	0.759	0.766	0.859
10	50	0.522	0.757	0.774	0.780	0.868

If the law of corresponding temperatures holds, the values of T/T_c in each horizontal row should be identical. It is evident that neither water vapor nor methyl amine obey the law. The data for the remaining vapors indicate that the law of corresponding states does apply with close approximation to these vapors.

The Polanyi method of calculation, as modified by Berenyi,¹³ has been found to give approximately correct values for the magnitude of adsorption at various temperatures. The application and the discussion of this work will be left to a later paper.

SUMMARY

1. The adsorption isotherms have been determined at several temperatures for each of the vapors, methyl alcohol, ethyl alcohol, water, ammonia and methyl amine. The adsorbent was a uniform

¹³ Berenyi, Z. physik. hCem., 94, 628 (1920).

sample of a specially prepared, acid-washed, ash-free, steam-activated charcoal.

2. The isotherms for water vapor indicate that a different type of phenomenon is involved here than in the case of the other vapors. The retention of the water vapor by the charcoal is probably due to mere capillary action rather than to the surface forces of adsorption.

3. The Freundlich isotherm relation has been shown to apply, except near saturation, to the two alcohols and to ammonia, but not to water and methyl amine.

4. The Kayser equation, as used by Geddes, is applicable only within a narrow range, while the equation of Schmidt and Hintel, and that of Williams do not seem to apply in any range.

5. It is found that neither the Homfray nor the Freundlich equations for the isobars express satisfactorily the relations shown by the isobars.

6. The Freundlich isostere equation, for the special case where $\xi = 0$, applies with considerable accuracy, except at high temperatures.

7. The Ramsay and Young law is not applicable to these vapors.

8. The law of corresponding states holds approximately, except for water and methyl amine.

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BIOGRAPHY

Clarence Milton Knudson was born in Denver, Colorado, December 19, 1900. He attended the public schools of that city. His undergraduate work and also that for the first graduate degree were taken at the University of Denver. During the year 1921-22 he held the position of instructor in chemistry at that institution. Since 1922 he has continued his graduate work at the University of Iowa. In 1922-23 he held an appointment as graduate assistant in chemistry, and in 1923-24 he was research assistant in physical chemistry. He is a member of the honorary and professional societies of Sigma Xi, Phi Lambda Upsilon, Gamma Alpha, and Alpha Chi Sigma.

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